

**SPECIFICATION**

**TITLE OF THE INVENTION**

**SYNTHETIC FUEL COMPRISING COAL DUST, WATER AND A REACTIVE  
ORGANIC COMPOUND, AND A PROCESS FOR MAKING SUCH SYNTHETIC  
FUEL**

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# **SYNTHETIC FUEL COMPRISING COAL DUST, WATER AND A REACTIVE ORGANIC COMPOUND, AND A PROCESS FOR MAKING SUCH SYNTHETIC FUEL**

## **FIELD OF INVENTION**

The present invention is directed to a synthetic fuel, also referred to as synthetic coal. These fuels are useful in providing higher BTU content to fuel users, most often electric public utilities. The fuels involved also meets all requirements of Title 29 of the Internal Revenue Code.

## **BACKGROUND OF INVENTION**

Coal has been, since the early 19<sup>th</sup> Century, a commercially important fuel. Appropriately processed, coal is an excellent high BTU provider and is relatively inexpensive due to the fact that it is readily available in the United States. Coal is relatively abundant in the environment but its chemical composition may vary from deposit to deposit and state to state.

From the earliest days of the U.S. coal mining industry (ongoing to even today), the grinding processing of coal obtained by mine workers done at the mine head (or more recently inside the mine itself) has generated coal dust as a waste product. On average, approximately 5% of all coal mined becomes such an unusable waste. This dust is not desired by traditional coal customers, cannot be shipped without costly containment apparatus, and unlike the slag waste of metal processing, can not be stored as hills of slag waste of the type which surround steel, iron or smelting plants. Coal dust is a very fine powder and a mound of such dust is easily distributed by even small low velocity winds.

Another method had to be found in the 19<sup>th</sup> Century to control the waste and the method chosen then remains the method of choice in the 21<sup>st</sup> Century. For more than a hundred years the method of disposal of coal dust has been by the creation of sometimes natural, more often artificial, lakes of water into which the coal dust is dumped. The moisture in water coagulates the dust and prevents its blowing away. These lakes in time

have become known as coal "lagoons" - it is estimated that over a thousand square miles of such lagoons exist in America most of which are close to mining communities. They are concentrated in coal mining areas and in particular the states of Ohio, W. Virginia, Alabama, Pennsylvania, Virginia and to some extent Wyoming and the Dakotas.

Lagoons are essentially dead unused space hostile to fish and recreation and ugly reminders of America's past. Coal dust itself is also very human-unfriendly. It is the proximate cause of black lung disease, dirty living and working conditions and is poisonous to man, animals and fish.

Several decades ago it was first realized that the existing coal lagoons were leaking out into rivers, creeks and city water supplies and that such leaking was almost impossible to stop. Also the drying out of lagoons, a more common phenomena than once thought possible, often now results in "black dust" storms which damage existing structures and machinery and injure the quality of life in mining communities.

In response to the above, Senators from the states most impacted, with substantial support from Senators in other states where citizens have worked to put an environmental movement in place, amended the Internal Revenue Code in the late 1990's. The code now provides a tax credit of approximately \$25 up to \$28 a ton to companies that develop and sell synthetic fuel products using coal dust. The amount is substantial as it is in addition to the sales price for the product that such companies can charge their customers if the synthetic fuel product they develop is comparable to natural coal. Section 29 of the Internal Revenue Code was largely directed in this regard to the dust found in coal lagoons but also have been interpreted to include dust generated at ongoing coal mine production facilities. The tax credit will expire in 2008 unless it is found to be working to make a dent in the serious environmental problem it was passed to address. As of today, approximately 12 manufacturing operations have been certified by the IRS to make new synthetic fuel products using coal dust.

It is estimated that several millions of dollars in research monies has been spent by major and smaller companies, which has been undertaken since the tax law change referred to above. The tax law therefore has provided and driven an increased interest in the discovery of a method of providing a useful, commercial synthetic fuel using coal dust. Many companies have settled on tar as the ingredient to fix or bind the dust but this is not satisfactory to most utilities. Tar acts only as a simple glue, has a very low melting temperature, and remains defective in providing binding strength. Utilities appear to want an organic binder which adds BTU's to the coal dust, with no ash remaining after combustion, and want a strongly bound product (that looks similar to coal) and burns and can be stored like coal.

By synthetic fuel, or synthetic coal, we mean a fuel made from coal dust or fines.

The use of an organic binder composition for coal dust which when mixed in the coal dust in a small quantity, and compacted, forms a useful fuel, has been a long time goal of inventors but not ever successfully achieved. In general organic binder compositions have been found to have numerous drawbacks: e.g. they do not provide the binding force of useful inorganic binders, they do not impart drying to the coal dust which is often quite moist and very often fail to provide the necessary binding or green strength. Many inorganic binders, such as tar, have very low melting temperatures and on hot days decompose the synthetic fuel and can make it useless. Up to now most commercial synthetic fuels utilizing coal dust have used either an inorganic binder, usually a smectite clay or a petroleum derivative such as asphalt and tar. Many of these binders were selected even though they often, unlike organics, produced no (and often diminished) BTU benefit when the fuel was burned but also significantly increased the amount of ash waste that itself had to be stored or otherwise handled.

Among the prior art that is pertinent to the present invention are the following patents.

U.S. Patent No. 44,000 issued in 1861 to a Brooklyn, New York inventor during the Civil War describes a synthetic coal made from coal dust and wheat and corn starches, likely obtained from flour then available in New York City grocery stores.

U.S. Patent No. 1,121,325 shows the briquetting of coal dust by mixing dry coal and starch, heating with oil and steam, compacting and then drying the mixture product.

U.S. Patent No. 1,851,689 issued in 1932 shows asphalt and carbohydrate pastes such as corn starch as a emulsion binder for coal briquettes which are described or made from finely pulverized coaking soft coal.

U.S. Patent No. 5,009,671 disclosed that synthetic fuel can be made from coal dust mixed with starch, molasses and water.

U.S. Patent No. 5,916,826 discloses the briquetting of coal fines using binders produced by liquidifaction of biomass with fast pyrolysis tars and petroleum asphalt added to the mixture.

U.S. Patent No. 6,013,116 describe a briquetting binder composition for binding metal oxides or coal fines comprising 95% asphalt and a sodium carbonate pumping liquor.

Other representative patents show a wide variety of binders for coal dust: U.S. Patent No. 3,898,076 (paraffin wax); U.S. Patent No. 5,221,290 (smectite clay) including bentonite; U.S. Patent No. 4,659,374 (pitch and lignon sulfanates), U.S. Patent No. 5,698,007 (water soluble polymers and caustics) and U.S. Patent No. 6,071,325 (organic binders including water soluble polymers including guar gum and starches).

It also has been commercially known to use Gunning range clays, cement, fly ash and bag house dust as binders for coal dust including mixtures of such ingredients with starch.

## **SUMMARY OF INVENTION**

The present invention is directed to a synthetic fuel made of coal dust, water and a defined organic chemicals reactive with the coal dust to form a bond with the coal dust upon compacting to provide a product very similar but chemically different than coal. The inventive product surprisingly in some case provides higher BTU value than coal alone (up to 5 to 1000 BTU per ton more than counterpart coal), does not produce the waste ash at the users' facility of inorganic chemicals (and many organic chemicals such as tar) and when the organic chemical selected is a "water absorbing" reactive polymer not only solve a moisture problem of coal dust but by gives even more increased green strength.

## **DETAILED DESCRIPTION OF INVENTION**

The objective of the present invention is to provide a highly useful synthetic fuel that contains at least 90% coal dust. This invention also surprising provides synthetic fuel having higher BTU content than natural coal and uses as its main ingredient, coal dust, what up to now has been a waste product of ever increasing environmental harm and concern.

Such a fuel is advantageous because among other reasons (1) more coal can be shipped per unit volume; (2) the fuel is particularly effective for electric utilities; (3) utilities can use fuel as a direct replacement for coal at the same stage in their operations; (4) a tax advantage under IRS law can be obtained by use of the fuel, and (5) end users experience greater freedom (e.g., less moisture is associated with the synthetic coal than natural coal).

The invention has been found particularly useful in providing fuel for electrical utilities. The fuel often surprisingly has a higher BTU content then coal from the same mine and hence gives the utility more value for the same price. It is particularly advantageous to have a synthetic coal fuel ready for addition to the utility power system as a replacement for natural coal. Such a synthetic fuel may easily be incorporated, as a fuel supply, without the need for special handling equipment at the utility.

The present invention in one preferred embodiment is directed to a synthetic fuel using defined ingredients.

One embodiment of the invention is a composition, comprising:

- (a) at least about 90 wt.% of coal dust, about 90% of the particle size of which is 50 microns or less;
- (b) from about 0.5 to 8.0 wt.% based on the weight of the coal dust of one or more organic chemicals reactive with said coal dust; and
- (c) water.

In the inventive embodiments, element (a), coal dust, is either a waste product of present manufacture of coal at or near a mine site or obtained from a waste storage facility such as a coal lagoon. Naturally occurring coal dust can contain impurities - in calculation of the percentages above only the coal portion of the two types of coal dust, either of which can be used in this invention, is utilized.

According to the present invention, the composition preferably comprises from about at least 90% coal dust although the invention is effective for lower levels of dust. These are intended to be covered by the use of the word about. Blends of coal dust can be used. Preferably, the product contains about 95 wt.% coal dust or more.

The preferred type of coal dust for the invention is where most of the dust is fairly fine particles, i.e. about 90% of the particles in the dust are 50 microns or less. It however is to be understood that dust of a less fine consistency containing substantially higher amounts of larger particle sizes will also produce useful synthetic fuel according to this invention.

Element (b), reactive organic chemicals useful for this invention are any organic compound reactive with coal dust and include functionalized starches, monosaccharides,

disaccharides, polysaccharides, copolymers of sodium acrylates and acrylamide and mixtures thereof as described hereafter.

By reactive is meant that the organic chemical is capable of forming either a chemical bond, a bond by hydrogen bonding, a bond of Van der Waal forces or other types of bonding with the coal dust. Since coal is mostly carbon, surprising a very unreactive element in many cases, it is speculated that the organic chemical may in fact be reacting mostly with the small amount of impurities found in coal dust to form the unexpected strong binding forces obtained by this invention although carbon bonding cannot completely be eliminated as a scientific possibility.

Preferred additives for this invention includes functionalized starches along with their salts and its esters.

Starch is a carbohydrate polymer having organic repeating units. Starches vary largely in the number of the repeating units in the polymer, which to a major extent depends on the source of the starch. Starch is normally composed of about 25% amylose and 75% amylopectin. Amylose is considered by scientists as a mixture of linear and slightly branched molecules whereas amylopectin is considered a densely branched, high molecular weight molecule. In some cereal starches, the amylose content can be as low as 0-1% as in waxy barley, waxy sorghum, and waxy corn and can be as high as 50-70% in some corn hybrids. Starch is often described as a repeating polymer of glucose units linked together by glycosidic bonds.

Starch is a polysaccharide obtained from plants, of which wheat, corn, potato, tapioca and rice are common commercial sources. Without the functionalizing modifications discussed herein, starch is a white, semi-crystalline, tasteless powder often in granule form. When starch is mixed with hot water in sufficient amount, such as at a temperature of 65°C or higher, irreversible gelatinization can occur. A large number of pure starch grades are available including those commonly referred to as commercial, powdered, pearl, laundry, technical and edible.



The starch for this invention must be functionalized to have moieties reactive with coal. Based on the disclosure provided herein, one skilled in the art will easily be able to formulate and select functional starches which are suitable for the present invention.

Examples of suitable modifications for functionalize the starches for use in this invention include cross-linking, substituting functional groups on the polymer chain, oxidizing, and acid-thinning.

Preferably, the starch is modified by well known oxidizing techniques. The Code of Federal Regulations, which is incorporated herein by reference, describes in detail modified starches intended for industrial applications. For example, 21 CFR 172.892 describes modification of starch for food use while 21 CFR 178.3520 covers the modification of starch for industrial applications.

Functionalized starch-based polymers useful for this invention preferably include reaction polyols derived from a reaction, using catalysts, of a starch with dibasic acids and hydrogen-donating compounds dissolved in a water slurry; the slurry is then subjected to high temperatures and pressures, yielding a low-viscosity polymer in an aqueous solution. Molecular rearrangement takes place, and the functionalized starch polymer formed are very different from natural starch in structure. The polymer can be further reacted with acids, bases, and cross-linking agents.

A water based solution and dispersion of a polysaccharide having a dextrose equivalent between 0 and 100, which also may contain inorganic salts and/or organic solubles. The polysaccharide itself may also be chemically modified. Preferred type of these products include the commercial (polysaccharide resins) products of Lorama Chemicals Inc.

A especially preferred functionalized starch additive is selected from Lorama's polysaccharide resins (CAS#65996-63-6) of the group consisting of JK270, JA250-3,

ECO plus ANECO. These resins are a water solution of a polysaccharide having a dextrose equivalent between 0.1 and 100 where the polysaccharide has been chemically modified.

More preferred additives for this invention are copolymers of sodium acrylates acrylamides. These are prepared by well known reaction processes, defined in the literature, and are commercially available products. Such compositions usually contain small amounts of impurities such as acrylamide, acrylic acid and 1-propenamide. Such copolymers also may be in a water solution.

Ciba Specialty Water Treatment Chemicals offers for sale a line of homopolymers, copolymers, and terpolymers based on acrylate, acrylamide and sodium acrylate very useful for this invention. The most preferred copolymer in this line is Ciba's Magnafloc 155 (CAS# 25085-02-3).

A particularly preferred organic composition is a mixture in a wide range of proportions of a functionalized starch and a copolymer of sodium acrylate and acrylamide. In general, the use of these type chemicals surprising results in a bond between themselves and the coal dust, which because of its nature, assures that the synthetic fuel can be stored at any high ambient temperature without degradation in green strength.

Element (c) is water.

It should be understood that the synthetic coal in many cases can include other materials but the preferred embodiment is where the above three ingredients form from more than 90% of the synthetic fuel up to 100% of the synthetic fuel.

The compounds of this invention are speculated to work by having the organic additive chemisorbed on the coal dust particles upon exposing the organic compounds to coal dust and water. It is further believed that the additives form a negatively charged

layer on the coal dust by each dust particle. It is also speculated that the additives, when burned with the coal dust, not only provide energy from their own nature as an organic product but also cause the coal dust itself to burn more completely and leave less residue. It is also speculated that the additive itself may react with the water in the mixture to form a combustible substance which adds to the BTUs produced when it burns. This synergesis is believed responsible for the increase in BTU content of the inventive product shown in the experimental results described below.

In another embodiment, the invention is directed to a process of making a synthetic fuel comprising a method of making synthetic fuel composition, comprising:

- (a) mixing at least about 90 wt. % of coal dust, 90 wt. % of the particle size of which is 50 micron or less and water with one or more organic reactive chemical to form a composition; and
- (b) compacting the composition;

thereby forming the synthetic fuel composition.

According to the present invention, several approaches are available to the production of the synthetic fuel. For example, one could disperse either unbeneficiated (i.e. coal dust with impurities) or beneficiated natural coal dust with the organic additive of this invention in water. Alternatively, coal dust and the additive can be premixed and added to the coal dust and dispersed. The resultant mixture is then compacted using a wide variety of known compaction, extrusion or other devices.

All in all, 12 synthetic coal plants have been approved by the Internal Revenue Service under Title 29 with total annual capacity of up to 15 million tons. Even with the relatively small levels of organic chemicals to coal dust required by this invention, up to 1 to 2 million tons of such additives are needed each year to fill the demand.

MCN Energy Group has recently opened 6 "coal fine" plants using manufacturing equipment that can produce synthetic coal according to the present invention. The

compacting briquetting apparatus at these MCN plants prepares coal dust briquettes using compacting forces up to 10 tons per square inch.

Each of the MCN plants has a rated annual capacity of one million tons of synthetic coal briquettes but actual production rates could be much higher, and cannot be accurately estimate until some months of operating experience is gained. The plants are at Monongalia County (2 plants), West Virginia, McDowell County, West Virginia, Knox County, Kentucky and Harrison County, Ohio.

The following examples are provided to illustrate our invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the claims.

#### **EXAMPLES:**

##### **Example 1**

##### **Technique**

A sample was prepared. The sample mixed 1 lb. of Ciba Magnafloc 155 with 2000 pounds of ground pond creek clean coal, ground to a particle size where about 90% of the particles were less than 50 microns. The Magnafloc 155 was mixed with water until fully hydrated – removal time is 3 to 10 minutes. After removing it was added to the coal dust and fully mixed. The mixture was then compacted using a 2 ton press.

The sample prepared above were compared with Pond Creek Clean Coal base coal, i.e. raw untreated coal, and the following results obtained:

	Pond Creek Coal	Inventive Sample
% Moisture	9.06	less than 1.00
% Sulfur	0.94	1.03
BTU/lb	12333	13452

## **Example 2**

An analysis was made of the synthetic fuel sample at a loading of 5% to the amount of coal dust with a small amount of water.

The process blended the parent coal with a binder to make a synthetic fuel product. Technical information was then obtained from a series of tests on the synthetic fuel and the parent coal and binder described below.

### Objective

The objective of performing analytical tests summarized herein was to determine if the process used to manufacture the synthetic fuel had significantly altered the chemical structure of performing certain types of analyses. The tests performed on the samples were selected due to their ability to determine differences in chemical structure and relatively common use of the tests.

### Procedures

Portions of the parent coal, organic chemical, and synthetic fuel products were obtained and prepared for analysis. A series of tests, including Fourier transformed infrared (FTIR) analysis, thermo-gravimetric analysis (TGA), ASTM proximate analysis, and heating value determination were performed on the samples.

The inventive product sample was compared with an analysis of a simple mixture of parent coal and binder (obtained from a mass weighted average of the results for the parent coal and binder) and was performed to determine similarities and differences. Significant changes would indicate that a chemical interaction among the components had occurred as a result of the manufacturing process.

## Tests Used

### A. FTIR Analysis

Fourier-transformed, infrared (FTIR) spectroscopy is a non-destructive analysis that probes the functional group content in coals. "Functional Groups" refers to chemical species bonded to aromatic carbon ring structure sites where chemical reactions commonly take place. They include different hydrogen types (i.e., hydroxyl, aromatic, and aliphatic hydrogen), vibrations due to the absorption of infrared radiation by functional groups with characteristic absorption bands (ref. 1).

For extremely complex molecular structures such as coal, detailed quantitative analysis using FTIR becomes difficult because of the overlap of peaks. However, comparison of spectra provides valuable information and can reveal structural differences between samples.

For FTIR analysis, a sample is imbedded in potassium bromide (KBr) pellets. Light in the infrared frequency range ( $400\text{--}4000\text{ cm}^{-1}$ ) is passed through the pellet. The sample absorbs specific light frequencies depending on the type and quantity of chemical bonds present. A list of absorption peaks of key functional groups commonly found in coals is listed in Table 1 (based on ref. 1).

For FTIR analysis of samples of the parent coal, and the synthetic fuel product all spectra were normalized for comparison purposes and are averages of sixteen separate scans of the samples used to produce them.

In general, the FTIR spectral region from  $4000$  to about  $1800\text{ cm}^{-1}$  identifies strong triple bonds and also hydrogen stretching. The range of about  $1800$  to  $1400\text{ cm}^{-1}$  corresponds to aromatic structures and double bonded structures. Wave numbers from  $1000\text{--}400\text{ cm}^{-1}$  identify single bond structures including various types of aromatic substitution bonding.

Comparison of the spectra for the synthetic fuel product with that determined for a corresponding simple mixture of the parent coal and binder was obtained. Changes in absorption peak areas for the fuel products, representing key chemical functional groups, relative to the corresponding simple mixtures, provide an indication of the degree to which the coal dust had been altered as a result of the organic chemical manufacturing process. Computer-measured areas of key samples are normal and depends on sample homogeneity and sample preparation. Previously performed statistical analyses on multiple coal samples indicate that, in general, peak area differences of greater than 20% represent a significant change in the functional groups indicated. As indicated in Table 2, the product sample shows significant variation in FTIR measured peak areas relative to the parent materials in the hydroxyl groups, aromatic CH, aromatic rings, cyclic CH<sub>2</sub>, C-O bonds, alkenes, aldehydes, polycyclic aromatic skeletal structure, aromatic substitution, ketones, and carbonyl groups.

This direct measurement of chemical structure indicated that chemical changes in these functional groups found in the product are significantly different relative to the parent coal material.

#### B. TGA Analysis

Thermo-Gravimetric analysis (TGA) measures the temperature and rate at which pyrolysis products evolve. The temperature required to break chemical bonds and subsequently release volatile fractions of the coal is determined by the strengths and types of bonds present. Volatile components, which are attached to coal macromolecules by weak chemical bonds, evolve at low temperatures. Components held with stronger bonds, which require more energy to break, evolve at higher temperatures. Differences in TGA curves (obtained under identical conditions) between a simple mixture of any ingredients and the corresponding product would indicate that changes in chemical bonding of the volatile components to the coal macromolecular structure had occurred.

Table 1. Absorption Bands of Functional Groups Common to Coals.		
Approximate wave number of absorption band in $\text{cm}^{-1}$	Characteristic Functionality	Normal presence or absence in coal and other carbonaceous materials
3330	OH groups	Present
3000	Aromatic CH	Present
2900	Aliphatic CH	Present
1720	Free C=O	Absent in coal present in lignite and humic acid.
1660	Isolated C=C	Typically absent
1600	Aromatic ring, possibly enhanced by conjugated OH-bonded C=O groups.	Present
1520	Aromatic ring	Absent in coal Present in lignite
1460	Aliphatic $\text{CH}_2$ and $\text{CH}_3$	Present
1370	$\text{CH}_3$ , cyclic $\text{CH}_2$	Present
1250 1170 1030	Three bands representing the polycyclic aromatic skeleton	Present in coal, absent in lignite and brown coal
540	Thiophenes, carboxyl groups and heterocyclics	Present
470	Branched and cyclo-alkanes and aliphatic ethers	Present



Table 2. Comparison of FTIR Results Parent Coal and Inventive Fuel Product				
Absorption peak wave number in $\text{cm}^{-1}$	Possible peak identification	Peak area for parent feed	Peak area for fuel product	Percent change
3242	Hydroxyl groups	57.2471	37.5598	52
3037	Aromatic CH	1.4065	1.7845	27
2917	Aliphatic CH	31.3838	32.0041	2
1599	Aromatic ring enhanced by OH bonded C=O group	85.4385	66.0679	29
1437	Aliphatic CH <sub>2</sub> and CH <sub>3</sub>	23.9114	21.9184	9
1370	Cyclic CH <sub>2</sub>	0.7088	0.4996	42
1259	C-O and -C-O-C-	0.6063	0.8038	33
1162	C-O and -C-O-C-	3.4685	3.7529	8
1030	C-O and Si-O	56.0891	42.5932	32
918	Alkenes, aldehydes	1.5229	0.9234	65
861	Polycyclic aromatic skeletal structure	0.8858	1.1594	31
801	Polycyclic aromatic skeletal structure	4.4407	4.1666	7
753	Polycyclic aromatic skeletal structure	1.2741	1.4457	13
695	Aromatic substitution	1.3672	1.8500	35
536	Carboxyl groups, thiopenes, heterocyclics	12.8038	10.9719	17
472	Branched and cyclo-alkanes and aliphatic ethers	10.2717	8.6162	19
427	Ketones, carbonyl	0.4702	0.7185	53
			Average	28

TGA tests presented herein were performed under inert conditions, using nitrogen as a carrier gas and with a heating rate of 15°C/min from room temperature to 700°C and pyrolysis rate curves for the inventive product and parent coal, respectively obtained. Pyrolysis weight loss rate curves for the parent coal/binder simple mixture and the fuel product were compared. The maximum rate of pyrolysis is significantly lower for the fuel product than determined for a simple mixture of parent ingredients suggesting increased chemical crosslinking in the fuel product. Quantitative differences in peak and high-temperature (668°C) pyrolysis rates for the coal/binder mixture and fuel product are

given in Table 3. The accuracy of weight loss determination for the thermo-gravimetric analyzer used for these tests is 1%. Sample-to-sample variation can be 2-3% for non-homogeneous materials such as coal.

Differences in peak pyrolysis mass loss rates of 21% provides strong evidence of a significant chemical change in the synthetic fuel product relative to the parent materials.

Table 3. Pyrolysis Rates of Feed Materials and Fuel Product		
Peak Pyrolysis Rate		
Feed Materials (%/min)	Product (%/min)	Percent Change
2.12	1.76	21
High-Temperature (668°C) Pyrolysis Rate		
Feed Materials (%/min)	Product (%/min)	Percent Change
0.66	0.68	3

#### D. Proximate Analysis and Heating Value

Proximate analysis of the parent materials and synthetic fuel product is shown in Table 4. These tests were performed according to ASTM standard techniques (ref. 7). For purposes of comparing fuel structure, the results are presented on a dry, ash-free basis. The measurement error in reported results must be within the permissible limits to meet the ASTM regulations. Therefore, the permissible error limit results are used herein to provide a conservative indication as to whether measured differences are statistically significant.

Comparison of the dry, ash-free results for the fuel product to the simple ingredient mixture show the differences in volatiles and fixed carbon content are outside of the statistical error limitations ( $\pm 0.5\%$  for volatiles and fixed carbon). Therefore, these results provide additional evidence of chemical change in support of the FTIR and TGA results. The difference in the heating value is within the statistical error limitations ( $\pm 107$  BTU/lb for the heating value).

The proximate analysis shows that ash and sulfur levels were somewhat higher for the fuel product than for the parent materials. However, this is not thought to be a result of a chemical change, but possibly due to a mineral inclusion.

Table 4. Test Results for Parent Ingredients and Fuel Product (as received basis).				
Parameter	Parent Coal	Reactive Organic Compound	Simple Mixture	Fuel Product
Moisture	17.60	98.90	21.67	7.20
Ash	6.29	0.08	5.98	7.57
Volatile Matter	32.28	1.01	30.72	35.11
Fixed Carbon	43.83	0.01	41.64	50.12
Sulfur	2.44	0.00	2.32	2.87
Heating Value (BTU/lb)	10890	89	10350	12111
Volatile Matter <sup>1</sup>	42.42	99.19	42.46	41.19
Fixed Carbon	57.58	0.81	57.54	58.81
Heating Value <sup>1</sup> (BTU/lb)	14308	8802	14304	14211

<sup>1</sup>dry, ash-free basis

#### Discussion of Results

Independent tests performed on samples of parent materials (coal and binder) and fuel product made with 5% binder have shown that significant chemical changes occurred during the manufacture of the synthetic fuel product.

Chemical changes were suggested by FTIR analysis, which showed alteration of hydroxyl groups, aromatic CH, aromatic rings, cyclic CH<sub>2</sub>, C-O bonds, alkenes, aldehydes, polycyclic aromatic skeletal structure, aromatic substitution, ketones, and carbonyl groups. TGA tests showed significant differences in peak pyrolysis rate characteristics. Proximate analysis showed statistically significant differences in the fixed carbon and volatiles content.

These differences indicate that the chemical structure of the synthetic fuel product is significantly different than the parent coal materials from which it is made.

### **Example 3**

#### Technique

Two additional samples were prepared. The first sample mixed one pound of Lorama starch JK270 with 2000 pounds of coal dust using the technique of Example 1. A second sample was made using a mixture of ½ pound of CIBA Magnafloc 155 and ½ pound of Lorama starch JK270 with a similar amount of coal dust to the first sample.

Similar tests as described above were conducted.

#### Sample 1

The FTIR spectrum for the additive was run. A comparison of the spectra for the fuel product with that determined for a corresponding simple mixture of the parent coal and additive was made. Computer-measured areas of key absorption peaks were listed and compared for the fuel product/simple mixture.

Comparison of the spectra of the samples showed significant variation in FTIR measured peak areas relative to the parent materials at the spectral location associated with aromatic CH, carbon-oxygen bonding, carbonyl, ketones, carboxyl groups, thiophenes, heterocyclics, branched- and cyclo-alkanes, aliphatic ethers, aromatic substitution bonding, and in the polycyclic aromatic skeletal structure. This direct measurement of chemical structure indicates that these functional groups are at a different concentration in the product compared to the parent materials. An average of the peak area differences of 38% for all of the peaks were determined. An average peak area difference of 38% provided evidence of a significant chemical change in Sample 1 product relative to the parent materials.

#### Sample 2

The FTIR spectrum for the 50/50 mixture was determined. A comparison of the spectra for the fuel product with that determined for a corresponding simple mixture of the parent coal and additive was made. Computer-measured areas of key absorption peaks were listed and compared for the fuel product/simple mixture.

Comparison of the spectra of the samples for Sample 2 showed significant variation in FTIR measured peak areas relative to the parent materials at the spectral location associated with cyclic CH<sub>2</sub>, carbon-oxygen bonding, alkenes, aldehydes, carbonyl, ketones, and in the polycyclic aromatic skeletal structure. This direct measurement of chemical structure indicates that these functional groups are at a different concentration in the product compared to the parent materials. An average of the peak area differences of 20% for all of the peaks was formed. An average peak difference of 20% provides evidence of a significant chemical change in Sample 2 synthetic fuel product relative to the parent materials with supporting evidence from additional testing.

#### TGA Analysis

TGA tests were performed on both sample under inert conditions, using nitrogen as a carrier gas and a heating rate of 15°C/min from room temperature to ca 700°C (ref. 7). Significant differences in the pyrolysis characteristics of the two sample fuel products relative to the parent materials, indicated modified cross-linking in the carbonaceous structure.

#### Proximate Analysis and Heating Value

A comparison of the proximate analyses of the parent coal dust material and the two synthetic fuel products were made. These tests were performed according to ASTM standard techniques. For purposes of comparing fuel structure, the results were presented on a dry, ash-free basis. The measurement error in reported results was within the permissible limits to meet the ASTM regulations. Therefore, the permissible error limit ranges provided a conservative indication as to whether measured differences are statistically significant.

Good correlation between the levels of ash and sulfur for the parent feed and synfuel product suggests that no significant processing or sampling errors likely occurred with the collection of these samples. This suggests that these samples are representative and therefore useful for this analysis.

### Discussion of Results

Independent tests were performed on samples of parent materials (Kentucky coal, and the Sample 1 and Sample 2 additives mixed with coal dust). Fuel products were made with different percentages of the additives. Based on previously performed statistically analyses, a value of greater than 25% in the average FTIR peak area difference indicates that a significant chemical change has occurred between the synthetic fuel product and the parent material. If the average peak area change is between 15-25% then results from other types of tests, such as TGA or proximate analysis, helps determine if the indicated differences from FTIR analysis represent significant chemical change or some type of sample variability.

The opinion was reached that test results on the Example 1 sample made with the additive of Example 1 suggest that significant chemical changes occurred during the manufacturing of the fuel product. FTIR analysis of the Example 1 fuel product sample and the corresponding parent materials indicates significant variations at spectral locations associated with cyclic CH<sub>2</sub>, carbon-oxygen bonding, alkenes, aldehydes, carbonyl, ketones, carboxyl groups, thiophenes, heterocyclics, branched- and cyclo-alkanes, aliphatic ethers, aromatic substitution bonding, and in the polycyclic aromatic skeletal structure. The proximate analysis test results for this fuel product show significant differences in the amount of volatiles and fixed carbon relative to the parent materials.

The opinion was reached that test results on the Sample 1 that significant chemical changes had occurred during the manufacturing of the fuel product. FTIR analysis of the Sample 1 fuel product sample and the corresponding parent materials indicates significant variations at spectral locations associated with aromatic CH, carbon-oxygen bonding, carbonyl, ketones, carboxyl groups, thiophenes, heterocyclics, branched- and cyclo-alkanes, aliphatic ethers, aromatic substitution bonding, and in the polycyclic aromatic skeletal structure.

The opinion was reached that the test results on the Sample 2 suggest that significant chemical changes occurred during the manufacturing of the fuel product. STIR analysis of the Sample 2 fuel product sample and the corresponding parent materials indicates that variations occurred in the FTIR measured peak areas relative to the parent materials at spectral locations associated with cyclic CH<sub>2</sub>, carbon-oxygen bonding, alkenes, aldehydes, carbonyl, ketones, and in the polycyclic aromatic skeletal structure. The TGA test results for this fuel product show significant differences in the peak pyrolysis rate characteristics. These differences obtained from different analytical tests indicate that the chemical structure of the Sample 2 fuel product is significantly different than the parent materials from which it is made.

In summary, the results of the analytical tests performed on parent materials and fuel products indicate that significant chemical changes have occurred in production of these synthetic fuel products. Good correlation between the levels of ash and sulfur for the parent feed and all of the synfuel products suggests that the fuel product samples are representative of the parent materials from which they were produced and therefore useful for this analysis.